

AD 686486

SEMIANNUAL TECHNICAL SUMMARY REPORT

15 April 1968 to 30 September 1968

EXTRINSIC PHOTOCONDUCTIVITY IN SILICON

R. B. Emmons
(415) 966-2667

Sylvania Electronic Systems - Western Division
Mountain View, California

30 September 1968

Contract No. N00014-68-C-0421

This document has been approved
for public release and sale; its
distribution is unlimited

14 June 1968 - 14 June 1969

Project Code No. 421

ARPA Order No. 306

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va. 22151

MAY 5 1989

E

ABSTRACT

A maximum impurity optical absorption cross section of $4 \times 10^{-16} \text{ cm}^2$ has been measured for Ga in Si. Based on this measurement and the thickness limitations of planar processing, estimated doping densities of $1 - 2 \times 10^{18} \text{ cm}^{-3}$ will be required for detector mosaics produced by planar techniques. The effects of these high doping densities on detector properties are discussed. Fabrication of Ga doped Si detectors in material doped to $2 \times 10^{17} \text{ cm}^{-3}$ is described. A peak D^* of $1.3 \times 10^9 \text{ cm (Hz)}^3/\text{W}$ is reported for these preliminary devices. A simple and versatile time constant measurement based on detector noise spectral density is discussed.

TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
1.0	INTRODUCTION	1
	1.1 Background	1
	1.2 Program Objectives	1
	1.3 Assignment of Responsibility	
2.0	TECHNICAL DISCUSSION AND RESULTS	3
	2.1 Extrinsic Impurity Density	3
	2.1.1 Required Impurity Density	3
	2.1.2 Impurity Absorption Cross Section	4
	2.1.3 Possible Influence of Impurity Band Conduction	10
	2.1.4 Detector Resistance	12
	2.2 Material Considerations	14
	2.2.1 Starting Material Purity	14
	2.2.2 Single Crystal Growth	15
	2.2.3 Epitaxial Growth	16
	2.2.4 Assessment of Metallurgical Influences	17
	2.3 Detector Fabrication	19
	2.4 Detector Measurements	19
	2.5 Time Constant Measurements	21
3.0	PLANS FOR THE NEXT QUARTER	23
4.0	REFERENCES	24

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1.	Transmission of Ga doped Si	8
2.	Optical Cross Section of Ga in Si $N_A = 2 \times 10^{17}$ cm ⁻³	9
3.	Ga Doped Si ρ as a Function of t	13

1.0 INTRODUCTION

1.1 Background

Extrinsic photoconductivity was originally discovered⁽¹⁻³⁾ and investigated⁽⁴⁻⁹⁾ in silicon in the 1950's. However, work on extrinsic photoconductivity shifted quickly to germanium, and for a number of years the only related work accomplished in silicon was peripheral.

The principal reasons for the shift of extrinsic detector development from silicon to germanium in the 1950's were the difficulties in obtaining silicon of the required purity at that time,⁽¹⁰⁾ and the lack of good techniques for making noise-free ohmic contacts to silicon⁽¹¹⁾. Difficulties with the purity of silicon and with contacting procedures have now been overcome in the semiconductor industry generally, as is evidenced by the almost total conversion of the transistor business from germanium to silicon. It is our conviction, which recent work supports,^(12,13) that these difficulties can now also be overcome in silicon extrinsic photoconductors.

What is perhaps more important, however, is the extent to which the stability of the oxidized silicon surface has made commonplace, through planar techniques, the production of very high densities of discrete devices on silicon wafers. The silicon vidicon photocathode recently announced by Bell Telephone Laboratories is an example of the impact these techniques can have on photosensitive devices. A variation of what was accomplished here with silicon intrinsic photoconductivity may also be possible with silicon extrinsic photoconductivity.⁽¹⁴⁾

1.2 Program Objectives

The first object of this program is to construct and evaluate heavily doped Ga and Al doped Si extrinsic photoconductors. The detector and material measurements made will emphasize possible problems associated with high doping densities (to $\approx 2 \times 10^{18} \text{ cm}^{-3}$) to determine whether background limited operation can be approached with these detectors. In addition to the highest possible sensitivity, these detectors are to have a measured frequency response to 500 MHz.

The second object of this program is to construct a 3 x 3 detector array using planar techniques. These detectors are to be parallel connected, each with a 500 MHz frequency response.

Section 2.1 of this report discusses the detector thicknesses compatible with silicon planar techniques, and describes experimental measurements of the impurity optical crosssection. These two parameters establish the range of required doping densities. The effects of these doping densities on detector design are then discussed, emphasizing the possible influence of impurity band conduction and the effect of impurity scattering in limiting the majority carrier mobility. Section 2.2 discusses material growth procedures, particularly as they affect the majority carrier recombination time. Sections 2.3 and 2.4 discuss detector fabrication and the measurements obtained on the detectors made to date. Section 2.5 discusses the method of time constant measurement being considered. Section 3 discusses plans for the next quarter.

1.3 Assignment of Responsibility

The principal investigator for this program is R. B. Emmons, Engineering Specialist. The program will be carried out under the supervision of M. B. Fisher, Manager of the Component Products Department of Sylvania's Electro-Optics Organization, Mountain View, California.

2.0 TECHNICAL DISCUSSION AND RESULTS

2.1 Extrinsic Impurity Density

2.1.1 Required Impurity Density

Our first task is to specify the impurity density levels that are required for the successful application of planar technology to extrinsic photoconductors. We are particularly interested in the 10-micron wavelength region because of the 8-14-micron atmospheric transmission window, within which lies the maximum radiant intensity of objects near room temperature, and because of the increasing importance of the efficient, powerful CO₂ laser emitting at 10.6 microns. To indicate the potential advantages of the extrinsic silicon detector, we may compare the Hg doped Ge detector now widely used for this wavelength region (sensitive to 14.3 microns) with the Ga doped Si detector (sensitive to 17 microns). The maximum solubility of Hg in Ge is in the range $10^{15} \text{ cm}^{-3} < N_A < 10^{16} \text{ cm}^{-3}$. This low solubility is characteristic of the elements of the group IIb elements in Ge. The cross section of these impurity centers for optical absorption, σ_{op} , is of the order of 10^{-16} cm^2 . Consequently, the maximum impurity absorption coefficient $\alpha_1 = \sigma_{op} N_A$ is in the range $1 > \alpha > 10^{-1} \text{ cm}^{-1}$. Thus in order to absorb enough of the light to obtain a good quantum efficiency, detector thicknesses of 1 cm or more are required. In practice, it is common to use Hg doped Ge detectors several millimeters thick and accept the reduced quantum efficiency.

In contrast, the solubility of the group III element Ga in Si is 10^{19} cm^{-3} (19). The maximum impurity absorption cross section of Ga in Si, as discussed in the next section, is $\sigma_{op} = 4 \times 10^{-16} \text{ cm}^2$. The impurity absorption coefficient of Ga doped Si may therefore be as high as $\alpha_1 = \sigma_{op} N_A = 4 \times 10^3 \text{ cm}^{-1}$. Thus it is in principle possible to absorb the majority of the incident light in a detector as thin as 2.5 microns.

It will not be possible however, because of impurity band conduction and low mobility, to use doping densities as high as 10^{19} cm^{-3} . Therefore, it is important to know what maximum thicknesses are compatible with the use of planar techniques in mosaic construction. In the design of a multielement

detector, one important limitation on the layer thickness will arise from the requirement for the minimum possible dead space between elements. Assuming that the starting material is an epitaxial layer of Ga doped Si on an n-type substrate, the Ga doped devices will be delineated by an n-type diffusion through the epitaxial layer. In this case, and very likely in any mosaic design, an impurity diffusion as deep as the detector thickness will be required during fabrication. However, it is difficult to obtain an element separation smaller than the depth of the required diffusion. Hence, if an element separation of 1 mil is required, the maximum device thickness will be of the order of 40 microns. On the basis of such considerations as the time required for an impurity diffusion and the quality of thick epitaxial layers, this 40 micron thickness is reasonable. Substantially thicker layers would present severe difficulties. Thinner layers are of course easier.

It is thus clear that doping densities in the range of 1 to $2 \times 10^{18} \text{ cm}^{-3}$ will be required in order to obtain the best possible quantum efficiencies and also allow the use of planar techniques for fabrication.

2.1.2 Impurity Absorption Cross Section

The thickness required for good quantum efficiency in an extrinsic photoconductor is determined by the impurity density and by the cross section of the impurities for optical absorption, where the impurity optical cross section is given in terms of the impurity absorption coefficient by $\sigma_{op} = \alpha_i / N_A$. The only reported measurements of the optical cross sections of column III impurities in silicon at energies above the activation energy are those of Burstein et al. (15). Since this data was obtained when silicon metallurgy was just beginning to produce good quality single crystals and since the optical cross section is of considerable importance in the optimum design of impurity photoconductors, it seemed important to confirm these early results by re-measuring the low temperature transmission of some suitably doped material.

In the design of the transmission experiment, an effort was made to minimize the effect of the lattice absorption lines which occur between 7 μm and 18 μm in silicon, and also to reduce the possible error caused by multiple reflections in the region of expected maximum absorption (10 μm to 16 μm). To reduce the effect of absorption by the lattice, a thin wafer (0.03 cm) of fairly heavily doped material ($2 \times 10^{17} \text{ cm}^{-3}$) was chosen. The maximum absorption constant due to a lattice vibration is at 610 cm^{-1} (16.4 μm), assigned by Johnson⁽¹⁶⁾ to a summation of one transverse optical and one transverse acoustic phonon. The magnitude of this absorption line is $\alpha_l = 45 \text{ cm}^{-1}$ at 20°K. Absorption constants for all the other lattice vibration absorption lines are less than 20 cm^{-1} . In contrast, from Burstein's data⁽¹⁵⁾, the impurity absorption constant for $2 \times 10^{17} \text{ cm}^{-3}$ material was expected to be of the order of 100 cm^{-1} . Since the absorption varies exponentially with α , little or no evidence of lattice absorption would be observed in the presence of impurity absorption for the sample parameters chosen.

Multiple reflections in a parallel plate of a high index material such as silicon can cause difficulties if the absorption is small. If the wafer is well aligned in a parallel beam, the transmission is given by

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{1-R^2 \exp(-2\alpha d)} \quad (1)$$

If the wafer is not well aligned in the beam, the transmission may be only

$$T = (1-R)^2 \exp(-\alpha d) \quad (2)$$

For silicon, the difference in transmission is 5% when α is small, a significant possible source of error. For the sample chosen, this source of error was minimized since the maximum absorption, which was of primary concern, was expected to be rather large. For the parameters given above, the denominator of Equation (1) will be no smaller than ≈ 0.99 between 10 μm and 16 μm . To obtain the transmission measurement, the 0.03 cm thick wafer of

optically polished silicon was secured to a heavy copper window mount on the tail of a He dewar using an indium "O" ring to insure good thermal contact. The clear area of the window was 3/8 inches in diameter. The opposing holes in the 77° cold shield and the outer jacket were also 3/8 inches in diameter. The windows used on the outer jacket were KBr, 0.635 cm thick. Transmission data was taken using a Perkin-Elmer Model 631 spectrophotometer. Although this spectrophotometer is a double beam instrument, the measurements were taken in a "pseudo" single beam mode. This method of operation was found necessary because the low transmission of the sample, and the vignetting of the sample beam caused by the He dewar, greatly limited the energy available in the sample beam. To obtain a good double beam signal it was necessary to similarly attenuate the reference beam. As a result of the low reference beam energy the zero level could not be maintained constant through the spectrum. A second run with the sample beam blocked was thus required to obtain an accurate "zero" level. The sample transmission was obtained by normalizing against this zero level.

Because of the limited energy available through the sample, it was decided not to attempt to obtain absolute transmission data from the spectrophotometer. The data obtained were instead assumed to be relative and were taken with the scale expanded to obtain the largest possible readings in the region of maximum transmission near 23 μm . The data was then made absolute by a separate measurement of the transmission at 10.6 microns using a CO_2 laser and an Eppley thermopile. The data were then corrected for the transmission losses in the KBr windows, which was measured separately using a Beckman IR-4 spectrophotometer with a KBr prism interchange. This transmission data was checked for consistency using the dispersion data given by Stephens⁽¹⁷⁾ for the spectral region where only Fresnel losses are important, and using the transmission data given by Mentzel⁽¹⁸⁾ from 20 μm to 25 μm . In removing the KBr window losses from the data, it was found that transmissions slightly greater than the theoretically possible maximum of 54% were indicated in the 24-25 micron region. Adjustment to obtain reasonable results indicated that the measured transmission data taken with the Beckman was only good to about 3% in this region. Fortunately this region of the spectrum is not of primary interest for the present work, and in the region of primary interest an accurate independent measurement using a CO_2 laser was available.

The transmission data obtained are shown in Figure 1. The curve shows a broad impurity absorption peak from about $10 \mu\text{m}$ to $16 \mu\text{m}$ having an apparent maximum at about $14 \mu\text{m}$ (0.09 eV). This maximum is at a somewhat longer wavelength than reported by Burstein, and appears to resemble the optical cross section of Al more closely than Burstein's measurements indicate. This is a reasonable result since these two impurities have very nearly the same activation energy. In addition to the impurity absorption above threshold, the lattice absorption band at $16.4 \mu\text{m}$ is observed, and five of the seven previously observed⁽¹⁹⁾ absorption lines due to the excitation of the gallium centers into their excited states have been resolved. No particular care was taken to obtain accurate results in this region of the spectrum since these absorption lines do not lead to photoconductivity. In addition, it is clear that these absorption lines are so strong that a reduction of the impurity density would be required if accurate data were required.

The impurity absorption cross section has been obtained from the transmission data of Figure 1 using Equation 1 and the relation $\sigma_{\text{op}} = \alpha_1 / N_A$, and is plotted in Figure 2 together with Burstein's data for comparison. The reflection coefficient of silicon was obtained from the dispersion relation given by Briggs⁽²⁰⁾, $n^2 = 1 + 10.695/[1 - (0.31/\lambda)^2]$. The shift in peak discussed above is obvious in this figure. The present data also indicates an absorption cross section whose maximum is 20% below that given by Burstein. Our data is believed to be accurate in the region of the peak to $\pm 5\%$. This estimated accuracy is based primarily on repeated measurements of the transmission at $10.6 \mu\text{m}$ which a CO_2 laser which yielded an average value of $T = 5.55\% \pm 0.5\%$. Conversion of this data to absorption cross section yields a value of $3.65 \pm 0.15 \times 10^{-16} \text{ cm}^2$.

The data of Figure 2 allows an optimum detector thickness to be chosen. For impurity concentrations in the range of 10^{18} cm^{-3} , the impurity absorption constant will be $\alpha_1 = \sigma_{\text{op}} N_A = 400 \text{ cm}^{-1}$. Thus for absorption of 86% of the light entering the detector an epitaxial layer thickness of $d = 2/\alpha_1 = 50 \mu\text{m}$ will be required.

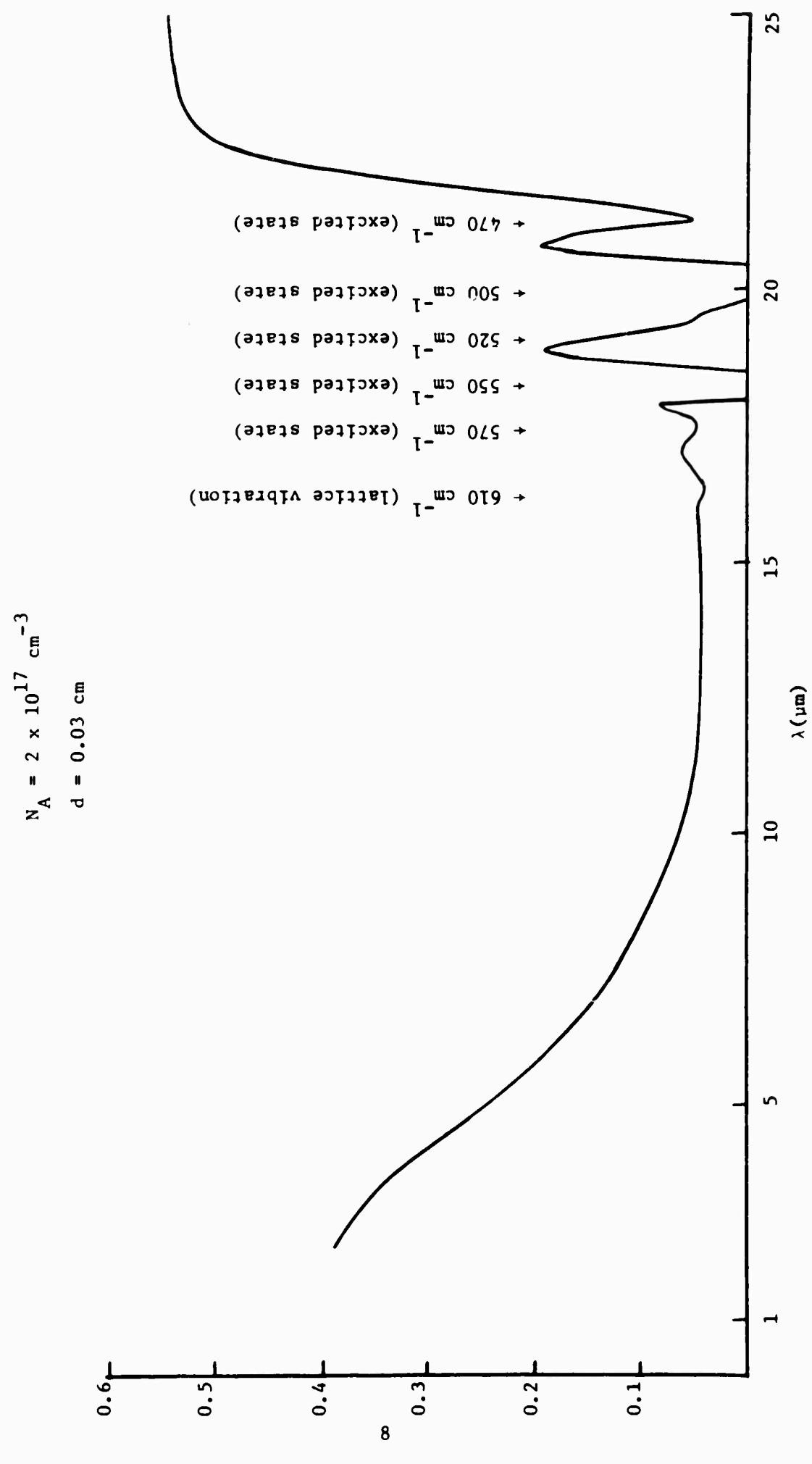


Figure 1 . Transmission of Ga doped Si

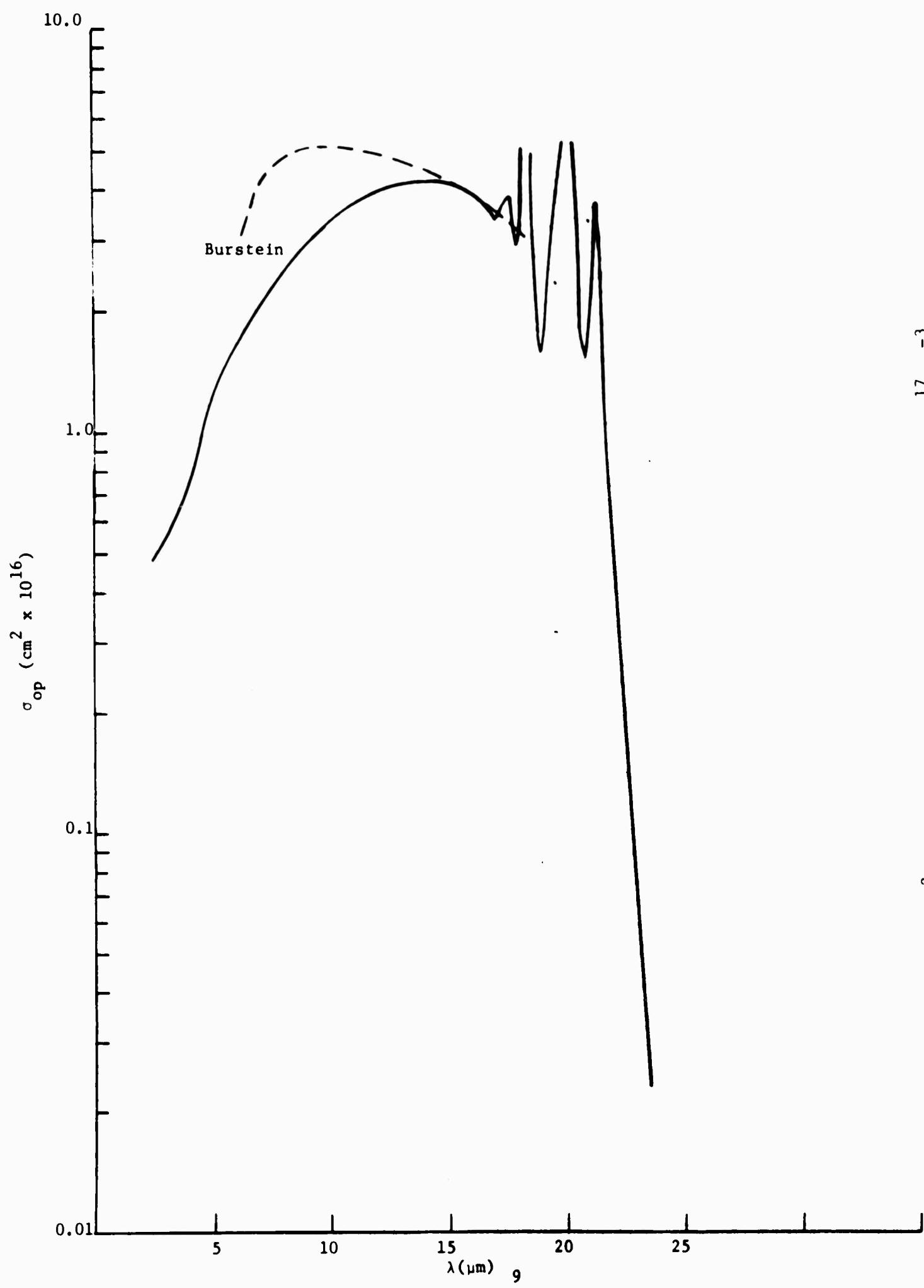


Figure 2 . Optical Crossection of Ga in Si $N_A = 2 \times 10^{17} \text{ cm}^{-3}$

2.1.3 Impurity Band Conduction

One of the questions which arises when moderate to heavily doped material is to be used for an extrinsic photoconductor is whether impurity band conduction, which begins to appear at large doping densities and low temperatures, will present any fundamental limitation to the operation of the detector. Optimum operation of an infrared sensitive photoconductor is usually considered to have been obtained when the fluctuations in carrier density which constitute the basic noise limitation on the detector sensitivity arise as a result of fluctuations in the background radiation incident on the detector rather than as a result of any fluctuation mechanism in the detector itself. To achieve this result, it is usually sufficient to cool the detector until thermal carrier generation is no longer significant in comparison to carrier generation by the background radiation.

If however impurity band conduction becomes significant before thermal carrier generation can be adequately suppressed, the situation is altered. The limiting noise in this case will be that associated with fluctuations in the impurity band conduction. This shift in the dominant conduction mechanism will have two consequences. First, the decrease in impurity band conductivity with temperature is slower than the decrease of conductivity due to thermal carrier generation. Hence, lower temperatures than expected may be required to achieve background limited operation. Second, the fluctuations in impurity band conduction may not be of the generation-recombination type, and it is possible that excess noise may be present when this conduction mechanism is dominant.

In order to judge the possible importance of impurity band conductivity, let us first consider the conductivity induced in an extrinsic Si photoconductor by 300°K background radiation, assuming an impurity activation energy of 0.070 eV. If the background is at 300°K , the number of background photons, Q , incident on the detector per cm^2 per sec is equal to the number emitted per sec by a one cm^2 black body at 300°K . If α_i , the impurity absorption constant is assumed independent of wavelength to $17 \mu\text{m}$ and zero thereafter, only those photons whose wavelength is less than $17 \mu\text{m}$ need be considered. Assuming approximately uniform carrier generation in the material, and a quantum efficiency η , the equilibrium carrier concentration in the material is

$$\rho = \frac{n_0 \tau}{d} \quad (3)$$

where d is the detector thickness and τ the majority carrier recombination time. If the detector is cooled sufficiently so that these background generated carriers constitute the majority of those present, the material resistivity will be

$$\rho = \frac{1}{p e \mu} = \frac{d}{n Q \tau e \mu} \quad (4)$$

where μ is the majority carrier mobility.

The quantum efficiency of the material is given by

$$n = \frac{(1-R) [1 - \exp(-\alpha_i d)]}{[1 - R \exp(-\alpha_i d)]} \quad (5)$$

where R is the reflection coefficient of silicon. Putting $R = 0.3$ and the thickness $d \approx 2/\alpha_i$, $n = 0.63$. If the detector has a 2π steradian field of view, $Q = 1.4 \times 10^{18} \text{ cm}^{-2} \text{ sec}^{-1}$. The resistivity is then, in terms of material parameters only

$$\rho = \frac{14}{\tau \mu \alpha_i} \Omega \text{cm} \quad (6)$$

The parameter τ is dependent on the donor compensation level rather than on the acceptor concentration and can be estimated fairly reliably at $\tau \approx 10^{-9}$ seconds (see Section 3). Both μ and α_i depend on the acceptor concentration. For material with $2 \times 10^{17} \text{ cm}^{-3}$ acceptors, we may estimate that $\mu = 10^3 \text{ cm}^2/\text{V sec}$ in the temperature range of $25-50^\circ\text{K}$ and $\alpha_i = 80 \text{ cm}^{-1}$. Thus we have for this material, $\rho = 1.8 \times 10^5 \Omega \text{cm}$. In order to obtain this value of resistivity with these sample parameters in the dark, cooling to a temperature of approximately 30°K is required⁽²¹⁾, and in material doped to $2 \times 10^{17} \text{ cm}^{-3}$, no evidence of impurity band conduction occurs. In order to confirm this, data were taken on the resistivity of $2 \times 10^{17} \text{ cm}^{-3}$ material as a function of temperature. The data are shown in Figure 3. The curve marked Sample A is most accurate. Between 45 and 55°K it has a slope of $0.070 \pm 0.002 \text{ eV}$ in agreement with the expected activation energy for Ga in silicon. An oxide was left on one side of this sample, and below 45°K , this oxide, or

an inversion layer produced by it on the silicon surface was sufficiently leaky to shunt the silicon. Sample B was prepared from an adjacent wafer from the same ingot, but was freshly etched before being placed in the dewar. This data indicates, in agreement with Ray and Fan that impurity band conduction is not a problem in $2 \times 10^{17} \text{ cm}^{-3}$ material under the conditions assumed here.

When the carrier concentration is increased to 10^{18} cm^{-3} , the impurity absorption coefficient α_i increases proportionately, and it would appear that the material resistivity required for background limited operation would also decrease. This is not strictly true however, since the mobility is, in this temperature range, determined by impurity scattering, and hence will decrease as the carrier concentration increases. In addition, for more heavily doped material impurity band conduction may occur at a higher temperature. Ray and Fan⁽²¹⁾ indicate the onset of impurity band conduction at $\rho = 10^4 \Omega \text{cm}$ in $2 \times 10^{18} \text{ cm}^{-3}$ material. Resistance versus temperature data will thus be required on the more heavily doped material as soon as it is obtained in order to determine whether impurity band conduction in this more heavily doped material will limit or prevent background limited operation.

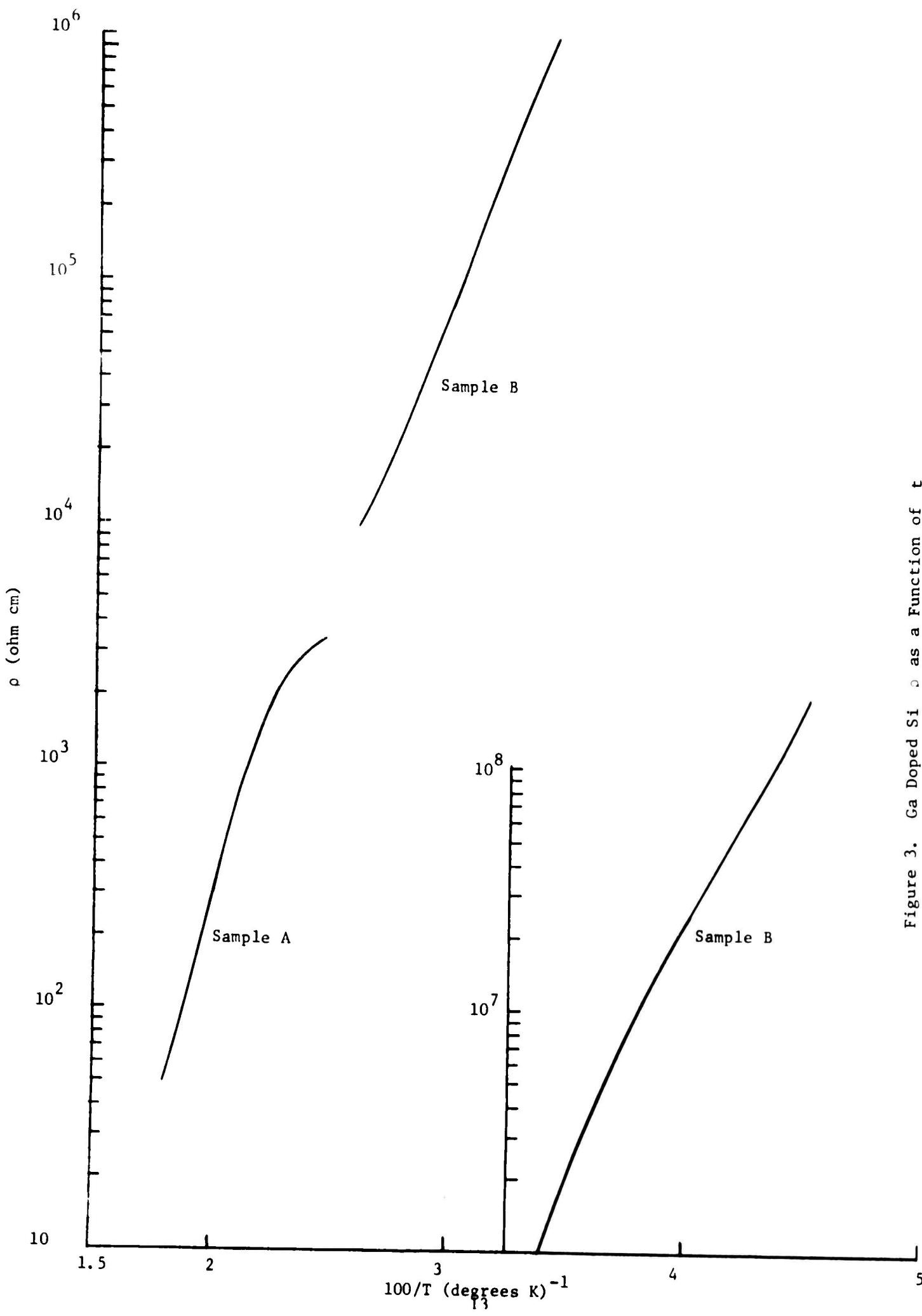
It should be noted that in this discussion a full hemisphere of 300°K background radiation was assumed. A significant reduction in background radiation, either by a large reduction of the acceptance angle, or by providing a cold background, will increase the detector resistance required for background limited operation and make the possible influence of impurity band conduction a matter of more serious concern.

2.1.4 Detector Resistance

The detector resistance to be expected for background limited operation is also restricted by the fact that the detector thickness is related to the impurity absorption coefficient. The resistance is given by

$$R = \rho \frac{\ell}{wd} \quad (7)$$

Figure 3. Ga Doped Si ρ as a Function of t



Substituting the resistivity given in Equation 6 , we have

$$R = 7.2 \times 10^6 \frac{\ell}{w} \quad (7)$$

Equation 8 contains neither the detector thickness nor the impurity absorption constant. An increase in the doping density, which reduces the material resistivity, also required a decrease in thickness for optimum design. As a result, detectors designed for background limited operation will not vary in sheet resistance except through the effect of doping density on mobility. Since, as we have noted, the mobility at low temperatures is determined by impurity scattering, the detector resistance may be expected to be somewhat higher than indicated in Equation 7 at doping densities in excess of $N_A = 2 \times 10^{17} \text{ cm}^{-3}$. The sheet resistance expected on the basis of these considerations is somewhat higher than convenient. The only technique which appears to be available to reduce the detector resistance, given the limitation on doping density required by planar techniques, is to change the detector aspect ratio; i.e., to make the detector short and wide ($\ell/w < 1$). This is possible while maintaining a square format through the use of interleaved comb electrodes if the detector is sufficiently thin. Such a structure is also entirely compatible with silicon planar technology, and experimentation with this type electrode structure is planned when thin epitaxially grown Ga doped material is obtained.

2.2 Material Considerations

It is well known⁽¹⁰⁾ that the response time of a cooled p-type extrinsic photoconductor is governed by the concentration of compensating donors in the material. To determine the range of time constants available in silicon, we comment briefly on silicon material purity and growth procedures, which determine the lower limit of the compensation available.

2.2.1 Starting Material Purity

The present basic limitation on the purity of polycrystalline zone refined silicon raw material is the difficulty in removing all of the boron. Dow Corning guarantees a boron content below $1.5 \times 10^{13} \text{ cm}^{-3}$ in its production

material and states that the material has a typical boron content of $5 \times 10^{12} \text{ cm}^{-3}$. For a premium price they will furnish material with boron content below $2.5 \times 10^{12} \text{ cm}^{-3}$. West German and Japanese suppliers have advertised silicon with boron content less than $1 \times 10^{12} \text{ cm}^{-3}$. Of course, boron is, like Ga and Al a p-type dopant in silicon. If one uses p-type B-doped Si as a starting material from which to make Ga or Al doped photoconductors, one must expect to deal with multiple acceptor effects in interpreting the photoconductive data⁽²²⁾. Although the relative contribution of the B to the observed photoconductivity would be small, it has seemed advisable to avoid this possible complication. If sufficient n-type impurities are present to more than compensate for the residual boron, the complication is avoided. In this case, the residual boron has no effect on the photoconductivity measurements⁽²²⁾. The penalty for removal of this complication is that this n-type impurity concentration in the starting material must be at least a factor of two larger than the minimum boron concentrations given above.

2.2.2 Single Crystal Growth

Two methods of preparing single crystals with a desired doping density from the polycrystalline starting material discussed above are common. The most common is the Czochralski method. When single crystals are pulled by this technique, the low concentrations of impurities discussed above cannot be maintained. The purest n-type crystals obtainable by this method have impurity concentrations of $5 \times 10^{13} \leq N_D \leq 1.5 \times 10^{14} \text{ cm}^{-3}$. The lowest boron content that can be maintained yields p-type crystals with impurity concentrations of $2 \times 10^{13} \text{ cm}^{-3} \leq 5 \times 10^{13} \text{ cm}^{-3}$. In addition, these crystals tend to have a high concentration of oxygen. Both the loss of purity and the high-oxygen content result from a small quantity of the crucible material being dissolved in the melt from which the crystal is grown. On the other hand, this preparation method has the advantages of simplicity and ease of doping, and results in crystals with a low dislocation density.

A lower basic impurity level can be maintained if the single crystals are prepared by the vacuum float-zone method used to prepare the raw material.

Using this growth procedure, p-type single crystals can be prepared with boron concentration of approximately $5 \times 10^{12} \text{ cm}^{-3}$ and n-type crystals can be prepared with impurity concentrations of approximately $2 \times 10^{13} \text{ cm}^{-3}$. These crystals also have a lower oxygen content, but have a higher dislocation density than crystals grown by the Czochralski method, and procedures for introducing dopants in the desired concentrations can be much more difficult.

Difficulties in the introduction of the desired Ga or Al concentration into a float-zoned crystal mitigate against the use of this technique at this time. Ga and Al are unusual dopants in silicon, principally because of their low segregation coefficients. This low segregation coefficient implies that most of the Ga tends to remain in the melt, the crystal being grown taking up only a small fraction. This fact, together with the small melt volume in the zone-leveling method, indicates probable difficulty in obtaining this type of material. Czochralski grown material is, on the other hand, available.

The consequences of the low segregation coefficients in the Czochralski growth method are two-fold. A fairly large range of resistivities and a practical dopant concentration maximum in the 10^{18} cm^{-3} range are to be expected in the pulled crystals.

2.2.3 Epitaxial Growth

The minimum impurity concentration in epitaxially grown layers is determined by essentially the same considerations which apply to Czochralski-grown material. Epitaxial material is grown by vapor-phase transport at high temperatures in quartz, and again boron and oxygen are picked up during growth. The highest resistivity generally quoted for n-type material is of the order of $100 \Omega\text{cm}$. Thus we can expect a background donor concentration of $N_D \approx 5 \times 10^{14} \text{ cm}^{-3}$ in any p-type material obtained by this process. Layer thicknesses and Ga or Al concentrations in the range required are however possible with this technique.

2.2.4 Assessment of Metallurgical Influences

Provided that the desired material can be grown with uniform and reproducible characteristics, which is true of the silicon being considered here, perhaps the most important influence of metallurgical problems on extrinsic photoconductivity is the effect of residual impurities on the time constant. In a p-type photoconductor, the time constant is determined by the rate of recombination of photoelectrically generated holes with negatively charged acceptors. At low-incident light levels and in the temperature range of interest, the acceptors are charged primarily by the electrons from the residual donors in the material. Thus, the time constant for p-type material is⁽¹⁰⁾ $\tau = 1/N_D \sigma_r v$, where N_D is the residual donor concentration, σ_r is the recombination cross section, and v is the thermal velocity of the free holes. We have indicated above that the minimum donor density in a crystal grown by the Czochralski method is in the range $5 \times 10^{13} \leq N_D \leq 1.5 \times 10^{14} \text{ cm}^{-3}$. Using the value $\sigma_r v = 10^{-5} \text{ cm}^3 \text{ sec}^{-1}$ we are led to expect maximum time constants from the Czochralski material in the range $5 \times 10^{-8} \geq \tau \geq 1.5 \times 10^{-9}$. Somewhat shorter time constants can be expected in epitaxial material. The value used for $\sigma_r v$ in this estimate is approximate, but consistent with the available information on doped Si. This parameter is however a function of temperature above about 10°K and has not been measured for Ga doped Si in the temperature range of interest.

It is obvious from the preceding discussion that making extrinsic photoconductors with a shorter time constant is easy from a metallurgical point of view. One simply increases the degree of compensation. The penalty is a decreased responsivity. However, the detector D^* is not influenced if the detector is background limited and if the signal level is not so low that a suitable amplifier cannot be found.

It is also clear from the preceding discussion that it is possible to make bulk Ga doped Si crystals with somewhat slower time constants. In this case, the metallurgical problem is slightly more complex. One would have to learn how to dope vacuum zone-leveled crystals heavily with Ga.

Residual donor levels of about $2 \times 10^{13} \text{ cm}^{-3}$ and time constants of about $2 \times 10^{-8} \text{ sec}$ might then be obtained. There is however no interest in this program in time constants longer than 10^{-9} sec . Hence, available material growth procedures would appear to be satisfactory.

2.3 Detector Fabrication

Since the final detector to be furnished on this contract will be a 3×3 element mosaic to be constructed by planar techniques, it was thought wise to begin the construction of all samples in this manner. Work was begun on material doped with Ga to $2 \times 10^{17} \text{ cm}^{-3}$. The wafers were nominally an inch in diameter and 20 mils thick. Masks were prepared to yield 6 detectors $3 \times 3 \text{ mm}$ and 4 detectors $2 \times 11 \text{ mm}$ from each wafer. The devices were fabricated as follows: The wafer was steam oxidized at 1000°C for 80 minutes to produce approximately 5000 \AA of SiO_2 on the surface. Photoresist was applied, and then selectively exposed and removed to allow a boron diffusion in the contact areas. Two diffusion processes have been tried to produce suitable contacts, a "box" diffusion, and diffusion from a "paint-on" source. These two techniques were used because of their inherent simplicity. We have hoped to avoid setting by a more complex gaseous diffusion of the type now commonly used in production. Following the diffusion, photoresist was again used to allow the oxide to be stripped from the contact areas. Al was then evaporated on the contacts, and sintered into the Si for 15 minutes at 600°C . The contacts were then cleaned again, and Ni plated to prepare them for soldering. Individual detectors were then cut from the wafer, the contacts were protected, the oxide removed, and the detector freshly etched before mounting.

2.4 Detector Measurements

Black body detector sensitivity measurements have been emphasized in the detector test program. The best 500°K black body sensitivities observed to date are approximately $5 \times 10^8 \text{ cm} (\text{Hz})^{1/2}/\text{W}$ at 30°K . These figures are more than an order of magnitude below those theoretically possible. Two current problems have been identified. The detector resistances are linear only to fields of about 60 V/cm indicating contact difficulties either with the boron diffusion or with the aluminum alloying. The theory upon which we are acting in the production of these contacts still appears sound. Our purpose is to obtain a heavy enough boron diffusion to insure degeneracy in the contact areas at the operating temperature. The aluminum alloy is to help insure that degeneracy and provides an ohmic transition to the contact metal. It would appear that practical problems in either the diffusion or the alloy process are causing the trouble. Work on the control and measurement of these contacting processes will continue.

The second problem is more easily remedied. The detectors measured so far have continued to increase in resistance and decrease in sensitivity as the temperature was decreased to 12°K, well below the expected background limited temperature. This problem has been traced to the fact that the detectors made to date have been too thick, (approximately five absorption lengths), and we have been illuminating the detectors from the side opposite to the contacts, which are on one face of the detector. We have thus inadvertently had a layer of unilluminated material between the face of the detector exposed to the light and the contacts. This excess material continues to increase in resistance as the temperature is lowered, and produces a resistance in series with the detector causing a substantial loss of signal. This problem will not of course exist in the detectors made in the epitaxial material, and will be remedied also in the experimental material currently in use.

These black body measurements will continue, and 10.6 micron measurements will be made as well. It is expected that well behaved detectors with black body sensitivities in the mid- 10^9 cm (Hz) $^{1/2}$ /W range will soon be available, allowing more extensive measurements of optimum bias, optimum operating temperature and more detailed measurements of contact properties.

2.5 Time Constant Measurements

Response times of photoconductors sensitive to $10.6 \mu\text{m}$ have been made using CO_2 lasers with GaAs electro optic⁽²³⁾ and Ge Bragg⁽²⁴⁾ amplitude modulators. Pulse response measurements have been reported using a GaAs electro optic modulator⁽²⁵⁾. Detector time constants have also been estimated from measurements with a Q-switched CO_2 laser and by observation of beats between longitudinal modes⁽¹³⁾. These various techniques all have disadvantages, and in the search for a simpler technique we have briefly considered the possibility of examining the power spectrum of the noise generated by $10.6 \mu\text{m}$ light falling on our photoconductor.

This technique requires that the noise generated by the unmodulated CO_2 laser light falling on the detector be mixed with the signal from an rf oscillator in an rf superheterodyne receiver. To estimate the sensitivity of this technique, assume that the rf receiver has an if bandwidth of 10 MHz, a maximum sensitivity of $\sim 120 \text{ dBm}$, and a 50 ohm input impedance. With such a receiver, a mean square noise current $\overline{i_n^2} = 2 \times 10^{-17} \text{ A}$ can be detected.

The mean square short circuit current due to generation-recombination noise in a photoconductor may be written

$$\overline{i_n^2} = \frac{4 e I_o G B}{(1 + \omega^2 \tau^2)}$$

where I_o is the current in the photoconductor, G is the photoconductive gain, B the noise bandwidth, and τ the detector response time. This expression may also be written in terms of the incident optical power as

$$\overline{i_n^2} = \frac{4 e^2 \eta G^2 B}{h\nu (1 + \omega^2 \tau^2)} P$$

For an estimated time constant of 10^{-9} sec , a photoconductive gain of 10^{-2} , and a quantum efficiency of 0.5, we have

$$\overline{i_n^2} = 3.2 \times 10^{-15} \frac{P}{(1 + \omega^2 \tau^2)}$$

Thus in order to maintain a signal-to-noise ratio of 10 dB in the receiver, 100 mW of CO₂ laser power would be required on the detector. This is a very high power level, but the laser can easily furnish it, and the detector can easily take it. The only question is whether or not this is an excessive heat load for the He dewar.

The heat load on the detector can be alleviated to some extent by chopping the light at a low frequency with a low duty cycle. Low frequency chopping is required in any case since the receiver in question will be of the phase-locked type. The feasibility of this experiment appears to be uncertain at this time, but is worth further examination. This type of experiment would allow as many points on the frequency response curve to be obtained as are required, simply by tuning the rf oscillator.

3.0 PLANS FOR THE NEXT QUARTER

Epitaxial material will be ordered. The He dewar will be modified for high frequency operation. The feasibility of the noise power spectrum frequency response measurement will be further examined. Work on detector fabrication techniques, and detector sensitivity measurements will continue.

4.0 REFERENCES

1. E. Burstein, U. S. Pat. 2, 671, 154; March 2, 1954, Application filed April 2, 1952.
2. E. Burstein, J. J. Oberly, and J. W. Davisson, NRL Report No. 3880 (1952), also, Phys. Rev. 89, 331, (Jan. 1953).
3. B. V. Rollin and E. L. Simmons, Proc. Phys. Soc. (London) 65B, 995, (1962), also, Proc. Phys. Soc. (London) 66B, 162, (March 1953).
4. R. Newman, Phys. Rev. 94, 1530, (15 June 1954).
5. R. Newman, Phys. Rev. 99, 465, (15 July 1955).
6. J. S. Blakemore, Canadian Jour. Physics 34, 938, (Sept. 1956).
7. R. O. Carlson, Phys. Rev. 104, 937, (15 Nov. 1956).
8. R. O. Carlson, R. N. Hall, and E. M. Pell, J. Phys. Chem Solids 8, 81, (1959).
9. R. S. Levitt and A. Honig, J. Phys. Chem Solids 22, 269, (1961).
10. E. H. Putley, Phys. St. Solidi 6, 571, (1964).
11. H. Levinstein, private communication.
12. R. B. Emmons and C. J. Repper, Final Report Contract No. Nonr-4848(00) (Dec. 1965).
13. R. A. Soref, JAP 38, 5201, (December 1967).
14. W. H. Crowell, T. M. Buck, E. F. Labuda, J. V. Dalton and E. J. Walsh, ISSCC Digest of Tech. Papers, pp. 128-129, (Feb. 1967).
15. E. Burstein, J. Phys. Chem Solids 1, 65, (1956).
16. F. A. Johnson, Proc. Phys. Soc. 73, 265, (1959).
17. R. E. Stephens et.al., JOSA 43, 110 (Feb. 1953).
18. A. Mentzel, Z. Physik 88, 178, (1934).
19. H. J. Hrostowski and R. H. Kaiser, J. Phys. Chem Solids 4, 148, (1958).
20. H. B. Briggs, Phys. Rev. 77, 727, (1950).
21. R. K. Ray and H. Y. Fan, Phys. Rev. 121, 768, (1961).
22. J. Blakemore, "Semiconductor Statistics," Pergamon Press, New York, 1962, Ch. 3.

23. C. J. Buczek and G. S. Picus, App. Phys. Letters 11, 125, (August 1967).
24. G. S. Picus and C. J. Buczek, Tech. Report AFAL-TR-68-102, May 1968.
25. T. J. Bridges et.al., App. Phys. Letters 12, 297, (1968).